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(54) Title: FLUORINE TREATMENT OF POLYOLEFIN FILMS (57) Abstract A thermoplastic polyolefin film having one or both surfaces of the film partially fluorinated to substantially increase wettability, printability, inkability is provided. A partially fluorinated thermoplastic stretch film of ethylene/acetate having increased cling and decreased block is also provided.		

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FLOURINE TREATMENT OF POLYOLEFIN FILMSCross Reference to Related Applications

This Application is a continuation-in-part of USSN
5 893,282, filed June 4, 1992.

Field of the Invention

The present invention relates generally to
10 thermoplastic films and, more particularly, to
partially fluorinated thermoplastic films especially
well suited for use in various applications.

Background of the Invention

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One type of polyolefin film, stretch/cling films,
is useful in a wide variety of fields including the
bundling and packaging of food and other goods. One
application of particular relevance to the present
20 invention is in the bundling of goods for shipping and
storage such as the bundling of large rolls of carpet,
fabric or the like for shipping. An important subset
of these bundling applications is in the containment
and unitizing of pallet loads. In such applications,
25 it is desirable that the film have cling properties to
prevent unraveling of the film from the pallet. The
tension in the stretched film may also cause the film
to be more susceptible to punctures and tears. It is
also desirable for polyolefin films, as a whole, to
30 have good stretch, tensile, puncture resistance and
tear resistance properties. Thermal stability of the
various film components is important for the recycling
of edge trim and film scrap generated in the various
film production processes.

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To impart cling properties to, or improve the
cling properties of, a particular film, a number of

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well-known tackifying additives have been utilized. Common tackifying additives include polybutenes, terpene resins, alkali metal stearates and hydrogenated rosins and rosin esters. The use of tackifying additives, however, may not be desirable. These additives have a tendency to accumulate on the stretch wrapping apparatus often requiring additional periodic cleaning and maintenance. They also can migrate into the bundled or unitized articles resulting in damage to such articles, as well as migrating throughout a film, even a multilayer film, causing tackiness on both sides. In palletizing operations, this may cause the film on adjacent pallets to cling together resulting in tear, puncture or other damage to the wrap and jeopardizing the integrity of the unitized load.

For this reason, it is desirable for stretch/cling type film to have slip or "anti-cling" properties on its "outer" side to prevent this interpallet cling. Slip is defined in terms of coefficient of friction. In other words, it is desirable that the "outer" side of the film have a low coefficient of friction in contact with another object, particularly another like film. As with cling, slip can be imparted to the film or improved through the use of various well-known slip, anti-cling and/or antiblock additives including silicas, silicates, diatomaceous earth and various lubricants.

In addition to conventional anti-cling additives, film cling properties can be altered by exposure to a corona discharge. The reactivity of discharge particles can alter the surface chemistry of the film and consequently its physical characteristics. The effect of such exposure can be observed by changes in film surface energy.

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More recently, the use of multilayer films has gained popularity. With a multilayer film, one can obtain a stretch/cling wrap having cling properties on one side and slip properties on the other side. (See
5 for example, U.S. Patent 4,518,654).

Other multilayer films comprising layers of the various aforementioned stretch/cling materials are disclosed in U.S. Patents 3,508,944, 3,817,821,
10 4,022,646, 4,082,877, 4,147,827, 4,189,420, 4,194,039, 4,303,710, 4,399,180, 4,364,981, 4,418,114, 4,425,268, 4,436,788, 4,504,434, 4,588,650 and 4,671,987; U.K. Patent Application 2,123,747; French Patent 2,031,801; and European Patent Application No. 0,198,091. These
15 multilayer films are generally produced by one of a number of well-known coextrusion processes also disclosed in the aforementioned references.

Many of the multilayer films, however, still
20 suffer from shortcomings possessed by their individual layers. For instance, most still require the use of tackifying additives to impart cling properties to the film. Others do not possess desired slip properties, particularly when in a highly stretched state. Still
25 others do not possess a desirable combination of stretch, tensile, tear resistance, puncture resistance and thermal stability properties.

It is known to treat various polymer surfaces by
30 fluorination. Materials like polytetrafluorethylene (PTFE) have been used extensively and have very low polar surface energies. As an alternative to fluorinated polymers like PTFE which are relatively expensive, localized fluorination at the polymer
35 surface has been used to reduce cost.

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U. S. Patent 3,740,325 to Maulon discloses a material and process for making a surface fluorinated material. The treated material is said to have greater water resistance, corrosion and soil resistance and be
5 more like PTFE.

U. S. Patent 3,647,613 to Scotland discloses a surface fluorinated high density polyethylene used for making containers suitable for storing hydrocarbons.
10 The HDPE surface containing a concentration of 0.01 to 30 micrograms of fluorine per square centimeter was said to improve permeability characteristics to gasoline.

15 U. S. Patent 4,880,675 discloses plastic containers comprising a polyethylene inner layer coextruded with a polypropylene outer layer wherein the inner layer is treated with a reactive fluorine source. Such treatment is said prevent the absorption of flavor
20 or aroma compounds by the container lining.

U. S. Patent 4,743,419 to Bierschenk discloses an on-line method for continuous fluorination of a polymer film while the film is being extruded.

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U. S. Patents 4,264,750 and 4,404,256 to Anand et al. disclose a process for making fluorinated low energy polymer surfaces by exposure to ions or radicals of fluorinated species in a cold plasma and polymers
30 having a substantially completely fluorinated surface of low surface energy which is substantially oxygen free.

Surface fluorination of high density and low
35 density polyethylene films between 40 degrees C and 100 degrees C is described by Volkmann et al. in Makromolecular Chemie, Macromolecular Symposium, Vol.

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25, pp. 243-248 (1989). The reaction is said to be diffusion controlled with the degree of fluorination increased by greater F₂ concentration in the fluorinating gas mixture.

5

Processes for surface fluorinating polymer films have been observed to introduce oxygen into the surface as a reaction byproduct when reaction times are smaller than those required to achieve complete surface fluorination. Anand et al. attributes this fact to a post-reaction with atmospheric oxygen or oxygen impurities possibly due to radicals trapped in the subsurface or some unreacted bonds on the surface. At any rate, this phenomenon is not generally observed following complete surface fluorination.

15

The presence of oxygen following a partial fluorination of a polymer surface increases surface energy, particularly the polar component, making the surface more adherent. Milker and Koch, "Surface Pretreatment of Polymer webs by Means of Fluorine"; and Milker and Koch, "Fluorine Makes Plastics Flexible"; describe a fluorination process for producing polymer films said to have good adhesion properties. The process is said to alter the surface on a more or less permanent basis so that the polar character of the material is increased.

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Summary of the Invention

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The present invention resides in part in the discovery that the properties of a polyolefin film are surprisingly enhanced following partial fluorination of one or both exterior surfaces of the film. Broadly the treatment comprises exposing one or both surfaces of the film to a dilute mixture of a fluorination species in a carrier gas for a time period less than that

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required to achieve complete surface fluorination and subsequently exposing the partially fluorinated film surface to oxygen.

5 In one embodiment, the present invention provides a thermoplastic film having excellent cling properties, even without the use of a tackifying additive. In fact, it is desired with the present invention to omit the use of such tackifying additives, in one
10 embodiment, such that a cling layer is essentially free of tackifier.

 This invention further provides films with enhanced wettability, printability and/or inkability.

15

 The present invention further provides a multilayer stretch/cling film having excellent cling properties on one side and excellent slip properties on an opposite side, even in a highly stretched state.

20

 Still further, the present invention provides a multilayer stretch/cling film which, as a whole, possesses desirable stretch, tensile strength, puncture resistance, tear resistance and thermal stability
25 properties.

 Finally, the present invention provides a process for producing such polyolefin films.

30 Detailed Description of Preferred Embodiments

 One or both surfaces of the coextruded layers of a film are partially fluorinated to enhance properties. The fluorination reaction catalyzes an oxygenation by-
35 reaction upon exposure to air. The surface to be treated is exposed to a suitable source of reactive fluorine, such as, for example, fluorine-containing

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plasmas, fluorine-containing gas mixtures, fluorine dissolved in solvents, UV activated fluorine gas mixtures, and the like. For example, any of the equipment and methodology for fluorination described in
5 Volkman or Milker and Koch can be used. A preferred fluorination method is direct fluorination using a gas mixture of molecular fluorine in an inert carrier gas.

Processes for fluorinating one or both sides of
10 film material in either batch or continuous operations are known. In a continuous process, the film is introduced into a reaction chamber generally having special locks at either end so that the film may be continuously passed through the chamber without
15 permitting gas to escape. The locks typically have a low pressure seal provided by a vacuum pump. Fluorine is metered from compressed cylinders generally pressurized with the diluent gas to achieve higher fill pressure. Gas exiting the reaction chamber is
20 compressed, combined with makeup gas and recycled to maintain a steady gas flowrate through the reactor. An absorber may be used to remove HF byproduct gas from the recycle stream. Very pure nitrogen is provided as flush and diluent gas. Waste fluorine can be catalyzed
25 to hydrogen fluoride then absorbed by an absorbent such as calcium hydroxide.

The duration of the exposure to F_2 and air required to obtain the desired enhancement of
30 properties such as cling, slip, printability, ink retention and wettability depends on the conditions of exposure, the film composition and properties, F_2 concentration, etc. It is important that the fluorination reaction is not permitted to go to
35 completion, i.e. to replace a majority of the available hydrogen atoms attached to the carbon backbone. Fluorination is substantially complete if a majority of

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the available surface hydrogen atoms are substituted for fluorine atoms so that there is relatively little further fluorination upon further continued fluorine exposure. Partial fluorination is indicated by a
5 dispersive surface energy less than the corresponding polar surface energy, in contrast to a surface energy higher than the polar surface energy when complete surface fluorination is achieved.

10 In general, F_2 exposure times of from 1 to 30 minutes are suitable. Subsequent oxygenation of the film surface is generally instantaneous upon exposure to air, although exposure to oxygen can be extended to ensure complete oxygenation without adversely affecting
15 the desirable film properties.

The amount of F_2 needed to enhance properties is relatively minor. Cling and block are improved in some instances with a fluorine:carbon surface stoichiometry,
20 as low as 0.001, as determined by X-ray photoelectron spectroscopy (XPS). However, if the fluorine:carbon surface stoichiometry is too high, the surface may not become activated for reaction to oxygen, a low polarity surface is produced and cling is adversely affected.
25 The fluorine:carbon surface stoichiometry is preferably in the range of from about 0.001 to about 3.0, more preferably about 0.01 to about 1.0, more preferably from about 0.01 to about 0.15. The amount of oxygen bonds formed by the activated surface depends on
30 surface F/C stoichiometry and the substrate material. For polyethylene, a suitable O/C stoichiometry is about 10 % or greater. The extent of surface activation for any given substrate material (as represented by subsequent O/C ratio) is believed to undergo a maximum
35 at a specific degree of surface fluorination (i. e. F/C ratio).

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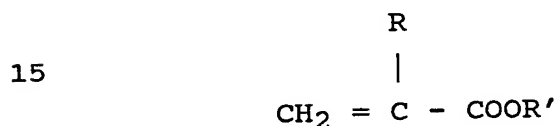
While not wishing to be bound by any particular theory, fluorination is thought to proceed by a radical mechanism by the abstraction of hydrogens. To the extent that some radicals produced do not react during the fluorination, subsequent reactivity with oxygen occurs. Oxygenation increases the polar surface energy which is a measure of hydrophilicity. The radicals can also react with carbons on neighboring chains producing a degree of surface crosslinking. Crosslinking reduces any tendency for interfacial diffusion (i. e. blocking).

Thermoplastic Stretch/Cling Films

Thermoplastic films produced in accordance with the present invention have excellent cling properties on the cling layer and slip properties on the non-cling layer. In a preferred embodiment, the use of tackifying additives can be avoided because of the excellent cling properties of the cling layer polymer against a partially fluorinated non-cling surface. The treatment while enhancing the cling property of the stretch/cling film does not, however, substantially increase the tendency to block, and generally a substantial decrease in the block is found. The non cling layer is preferably treated, however either side may be treated. The present thermoplastic films, as a whole, additionally have desirable stretch, tensile, puncture resistance and tear resistance properties. Further, the thermoplastic materials used for the cling and non-cling layers have excellent thermal stability, and edge trim scrap can be processed without significant loss of film performance. This combination of properties makes the thermoplastic films of the present invention especially well suited for use as stretch/cling wraps.

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The thermoplastic film preferably comprises a cling layer and a non-cling layer, wherein one or both of the exterior surfaces is partially fluorinated. The cling layer comprises a polymer of two or more monomers, wherein a first monomer comprises ethylene and a second monomer comprises an acrylate. Acrylate, in the singular, refers to both a single acrylate and combinations of different acrylates. These polymers will generally be referred to as ethylene-acrylate (or EA) polymers. Acrylates useful in the present invention are those of the general formula:



wherein R is selected from hydrogen or a hydrocarbon group having from 1 to 22 carbon atoms, preferably an alkyl, aryl, aromatic, olefin or the like hydrocarbon group and wherein R' is selected from the same or different of these hydrocarbon groups.

Preferred acrylates comprise those wherein R is selected from hydrogen or an alkyl group and wherein R' is the same or different of such alkyl group. Specific examples of preferred acrylates include methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, octadecyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and the like. Of these, methyl acrylate is particularly preferred.

In the preferred embodiment, the EA polymer comprises an acrylate content of between about 2% to about 40%, more preferably between about 10% to about 35%, most preferably between about 20% to about 30%,

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and especially between about 24% to about 28% by weight based upon the weight of the EA polymer. The EA polymer may have a wide range of melt indexes (MI), generally between about 0.1 to about 30 dg/min, more preferably between about 1 to about 10 dg/min (ASTM D-1238, Condition E).

The EA polymer may also comprise one or more free radically polymerizable monomers. Suitable examples include, but are not limited to, vinyl esters, acrylic acids (i.e. methacrylic and ethacrylic acid), other acrylates, carbon monoxide and the like. These additional monomers will generally be present in small amounts, usually less than a total of about 10% by weight based upon the weight of the EA polymer.

Optionally, tackifying additive may be added to the EA polymer during the polymerization reaction or subsequently blended in to improve the cling properties of the film. A wide variety of tackifying additives are well known in the art including, for example, polybutenes, atactic polypropylenes, terpene resins, hydrogenated rosins, rosin esters and other like hydrocarbon tackifying resins. It should be noted, however, that the aforescribed EA polymers produce films of sufficient cling so as to not require the use of a tackifying additive. The use of tackifying additives is contemplated by this invention but is not necessarily preferred. In a preferred embodiment, the EA polymer is essentially free of a tackifying additive.

The cling layer preferably comprises between about 5% to about 95%, more preferably between about 5% to about 35%, most preferably between about 10% to about 20% of the combined thickness of the cling and non-cling layers.

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The second layer of the multilayer stretch film comprises a non-cling layer opposite the cling layer. The non-cling layer comprises any suitable polyolefin or combination of polyolefins such as polyethylene, polypropylene, copolymers of ethylene and propylene, and polymers obtained from ethylene and/or propylene copolymerized with minor amounts of other olefins, particularly C₄-C₁₂ olefins. Particularly preferred are medium density polyethylene (MDPE), polypropylene and linear low density polyethylene (LLDPE), i.e., a copolymer of ethylene with up to about 20% by weight C₄-C₁₀ olefin(s). Especially preferred olefin comonomers include 1-butene, 1-hexene, 1-octene and 4-methyl pentene-1.

Suitable MDPEs include those having a density in the range of from about 0.92 to about 0.95 g/cc and a wide ranging MI, generally up to about 30 dg/min preferably between about 0.5 to about 10 dg/min.

Suitable LLDPEs include those having a density greater than about 0.900 g/cc more preferably in the range of from about 0.900 to about 0.940 g/cc. The LLDPEs may also have a wide ranging MI, generally up to about 30 dg/min, preferably between about 0.5 to about 10 dg/min.

Suitable polypropylene is normally solid and isotactic, i.e., greater than 90% hot heptane insolubles, having wide ranging melt flow rates of from about 0.1 to about 300 dg/min. As is known, such polypropylene is normally crystalline with a density range of from about 0.89 to about 0.91 g/cc for isotactic polypropylene. Employing polypropylene in the non-cling layer has the additional advantage of imparting abrasion resistance thereto.

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The non-cling layer preferably comprises between about 5% to about 95%, more preferably between about 65% to about 95%, most preferably between about 80% to about 90% of the combined thickness of the cling/non-cling layers.

Wettable, Printable, Inkable Films

Alternate embodiments of the invention provide wettable, printable and/or inkable polyolefin films.

The single or multilayer films as described above or other polyolefin films such as homo or co-polyethylene, homo or co-polypropylene, ethylene, vinyl acetate and the like may be partially flourinated to enhance wettability, printability and/or ink retention.

Wetting is the idea that maximum interfacial adhesive bond strength is achieved when the adhesive comes into contact with the adherend and the intermolecular forces across the interface are maximized. The partially flourinated films of this invention have increased wettability when compared to the non-flourinated films. Wettability is measured using standard treat solutions well known in the art (ASTM D2578-94). ASTM D2578-94 is hereby incorporated by reference. Wettability is also commonly reported in terms of polar surface energy which is measured by the geometric mean equation as shown for example on page 103 of Polymer Interface and Adhesion, Dekker Pub. 1982. hereby incorporated by reference. In essence, the partially flourinated film becomes more receptive to inks, dyes, pigments, adhesives, tackifiers, hot melt adhesives and the like yielding stronger bonds. The wettability of the partially flourinated film is

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substantially improved when compared to the non flourinated films. In preferred embodiments the partially flourinated films will have a polar surface energy of at least about 10 dynes/cm, preferably at least about 15 dynes/cm, even more preferably at least about 20 dynes/cm, even more preferably at least about 30 dynes/cm.

Thus, this invention contemplates partially flourinated films with adhesive compositions coated thereon for use in many applications such as tapes and labels. Suitable adhesives include hot melt compositions, pressure sensitive adhesive compositions, contact adhesive compositions and the like. Examples include EVA based hot melts, polyurethanes and polyacrylates.

This invention also contemplates films partially flourinated without adhesives used in a variety of applications such as packages, bags, containers and the like.

Likewise, the partially flourinated films are also more receptive to inks, dyes and other printing or coloring agents known to those of ordinary skill in the art including Fuchsine (CI 42510), Calcocid Greens (CI 44090), titanium dioxide, colloidal carbon, graphite, ceramics, clays, phosphor particles, metal particles and the like.

30

These agents may be applied by any of several methods known in the art, for example the pigment may be combined with a resin such as nitrocellulose or a polyamide and a solvent such as ethylacrylate or n-propyl alcohol to form a printing liquid that is then applied to a substrate. Rotogravure and Flurography are examples.

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The various films may also include one or more intermediate layers between the layers for any one of a number of well-known purposes such as, for example, to provide structural support, to modify the overall physical properties balance of the film, to utilize the recycle trim and scrap or to provide a barrier layer to oxygen or other gases. As just indicated, this intermediate layer may comprise the recycle trim and scrap, or may comprise any other suitable polymer. The intermediate layer(s), however, while preferred, is optional and should not be considered a limitation on the present invention.

The film layers of the present invention may, if desired, also include one or more other well-known additives such as antioxidants, ultraviolet absorbers, antistatic agents, release agents, pigments, colorants or the like.

Additionally, normal trim and scrap from the film production process, or from suitably recovered and reprocessed films can be recycled into layers, preferably the core structural layer of a three-layer film.

The EA polymers preferred for use in stretch cling films may be produced by any one of a number of well-known processes such as, for example, those described in U. S. Patent No. 3,350,372, which is incorporated by reference for all purposes as if fully set forth. Generally ethylene and any comonomers such as an acrylate to make an EA copolymer and, if desired, another monomer(s) are metered into, for example, a high pressure autoclave reactor along with any one of a number of well-known free radical polymerization initiators (catalysts) suitable for producing EA

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polymers. Particularly preferred catalysts include organic peroxides such as, for example, lauroyl peroxide, di-tert butyl peroxide, tert butyl peroxide and various azo compounds. Typically, the catalyst
5 will be dissolved in a suitable organic liquid such as benzene, mineral oil or the like. Ordinarily the catalyst is used at a level of between about 50 to about 20,000 ppm, more preferably between about 100 to about 250 ppm based upon the weight of the monomers.

10

MDPE, LLDPE and polypropylene may be made by well known Ziegler catalyst processes including gas phase, slurry, solution, and the like and are readily available commercially.

15

In preparing the thermoplastic films of the present invention, any one of a number of well-known extrusion or coextrusion (in the case of multilayer films) techniques as disclosed in the previously
20 incorporated references may be utilized. As preferred examples, any of the blown or chill roll cast processes as disclosed and described in those references is suitable for use in producing thermoplastic films in accordance with the present invention.

25

As previously mentioned, the thermoplastic films of the present invention have properties making them especially well suited for use as stretch/cling films, however this use should not be considered a limitation
30 on the present invention. For example, these films can be made into other forms, such as a tape, by any one of a number of well-known cutting, slitting and/or rewinding operations. Physical properties including, but not limited to, tensile strength, tear strength and
35 elongation can be adjusted over wide ranges by altering the resin types and specifications as appropriate to

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meet the requirements to a given wrapping, bundling or taping application.

For bundling, packaging and unitizing
5 applications, the thermoplastic film of the present invention is stretch-wrapped by any one of a number of well-known procedures (such as those disclosed in the
10 aforementioned incorporated references) around an article or a plurality of articles preferably so that the cling layer faces inside (towards the article) and the non-cling layer faces outside (away from the
15 article). Typical of articles suitable for bundling, packaging and unitizing with the present thermoplastic film include, but are not limited to, various foodstuffs (canned or fresh), rolls of carpet, liquid
20 containers and various like goods normally containerized and/or palletized for shipping, storage and/or display.

20 The foregoing more general discussion of this invention will be further exemplified by the following specific examples offered by way of illustration and not limitation of the above-described invention.

25 Examples

In the following examples, I/O cling is reported as the force in grams required to partially peel apart two strips of film. A first film strip is attached to
30 a 30 degrees inclined plane with the outside (O) surface (non-cling) facing upward. A second 1" X 8" strip is placed on top of the first strip with the inside (I) surface (cling) facing downward. Pressure is applied to the second strip to cause the two strips to
35 stick together. If an evaluation of cling under stretched conditions is desired, both film strips are prestretched and allowed to relax before testing. The

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end of the second strip at the base of the inclined plane is attached, by clip and string, to an apparatus which can exert a strain at a constant rate (Instron 1130). The two strips are then pulled apart at a crosshead speed of 10 cm/min until the aforementioned string is parallel with the base of the inclined plane. The force at this point is reported as cling.

Block is reported as the 180 degree peel strength of the outside surface (non-cling) of a first film specimen pressed with 200 psi at 154 degrees F (1.378 MPa at 103.3 degrees C) against the inside surface (cling) of a second film specimen for a specified length of time.

15

The block, cling or slip of multicompositional, multilayer films, refers to properties the film has when in physical contact with itself such as on a roll or a wrapped pallet. Such properties are generally referenced by noting the location of the surfaces or layers in contact (i.e. inside/outside (I/O)).

20

Examples 1-2 and Comparative Examples 1-6

A MDPE film was made from a resin having a melt index of 2 and a density of 0.92 g/cc produced in a gas phase reactor. The film was fluorinated using two different degrees of fluorination. One film had high fluorine concentration at the surface and the other a low fluorine concentration. Film surface stoichiometry for O/C and F/C as determined by x-ray spectroscopy (XPS) is given in Table I.

Fluorination was conducted by a commercial fluorination service which is believed to have used a conventional batch apparatus wherein the film substrate was exposed to a gas mixture of molecular fluorine in a

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pure nitrogen carrier gas for a set period of time in a reactor vessel. The fluorinated films were handled normally in air prior to physical testing.

- 5 To illustrate the effect of fluorine treatment on blocking tendency, film interfaces were prepared by pressing together a cling layer surface comprising a 24 % EMA film and a non-cling layer surface comprising the fluorinated MDPE described above. The pressing
- 10 conditions were 200 psi pressure and 158 degrees F temperature (1.378 MPa and 105.5 degrees C) for a set period of time. The blocking tendency was gauged by the peel force required to separate the films. As seen in Table II, interfaces made with both the low and high
- 15 fluorinated MDPE required very little peel force compared to the film interface lacking a fluorinated surface. Furthermore, the low fluorinated film interface was almost as resistant to blocking as the high fluorinated film interface.

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TABLE I
SURFACE STOICHIOMETRY

EXAMPLE	SURFACE	SURFACE STOICHIOMETRY		SURFACE ENERGY	
		O/C	F/C	DISPERSIVE	POLAR
1	MOPE	0.17	0.021	10.1	34.8
Comp. 1	MOPE	0.061	0.938	34.3	0.1

TABLE II
BLOCKING TEST RESULTS

EXAMPLE	FILM INTERFACE		PRESS TIME (min) ^a	PEEL FORCE (lb/in.)
	CLING LAYER	NON-CLING LAYER		
2	UNTREATED EMA (24 % MA)	Example 1	30	0.08
Comp. 2	UNTREATED EMA (24 % MA)	Comp. Example 1	30	0.01
Comp. 3	UNTREATED EMA (24 % MA)	UNTREATED MOPE	30	0.25
Comp. 4	UNTREATED EMA (24 % MA)	UNTREATED MOPE	5	0.28
Comp. 5	UNTREATED EMA (24 % MA)	UNTREATED MOPE	60	0.37
Comp. 6	UNTREATED EMA (24 % MA)	UNTREATED MOPE	120	0.53

a-200 psi/158°F press conditions (1.378 MPa and 105.5 degrees C)

Example 3 and Comparative Examples 7-8

Zero % stretch cling was measured for film interfaces prepared similarly to Examples 1-2 and Comparative Examples 1-6. The results were compared to a similar film wherein the interface surface was not

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fluorinated. As seen in Table III, the film interface (Example 3) having the low fluorine treated surface showed enhanced cling. The film interface (Comp. Example 7) having the high fluorine treated surface had very little cling, as expected.

TABLE III
CLING TEST RESULTS

EXAMPLE	FILM INTERFACE		CLING (g/in.)	
	CLING LAYER	NON-CLING LAYER	MAX	"AVERAGE"
3	UNTREATED EMA (24 % MA)	Example 1	358	288
Comp. 7	UNTREATED EMA (24 % MA)	Comparative Example 1	70	63
Comp. 8	UNTREATED EMA (24 % MA)	UNTREATED MDPE	284	241

The foregoing description of the invention is provided for illustrative purposes. Many variations and modifications of the invention will become apparent to those skilled in the art in view of the foregoing disclosure. It is intended that all such variations and modifications within the scope or spirit of the appended claims be embraced thereby.

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What is Claimed is:

1. A film comprising:
a mono-, bi- or multi-layered polyolefin film
5 comprising at least one partially flourinated surface
such that the wettability of the film is substantially
increased.
2. The film of claim 1 wherein the film has a
10 surface polar energy of at least about 15 dynes per
centimeter.
3. The film of claim 1, wherein the partially
flourinated surface is formed by exposure to flourine
15 and oxygen.
4. The film of claim 1 having an adhesive coated
thereon.
- 20 5. The film of claim 1 having one or more inks,
dyes, pigments or mixtures thereof affixed thereon.
6. The film of claim 1 further comprising ink
printed thereon.
25
7. The film of claim 5, wherein the pigment is
titanium dioxide.
8. The film of claim 1, wherein the flourinated
30 surface(s) has a flourine:carbon surface stoichiometry
as determined by x-ray photelectron spectroscopy of
from about 0.001 to about 3.0.
9. The film of claim 8, wherein the
35 flourine:chlorine stoichiometry is about 0.01 to about
1.0.

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10. The film of claim 1 further comprising a core layer.

11. The film of claim 9 wherein the core layer is
5 selected from the group consisting of linear low density polyethylene, recycled polyolefins, polypropylene, or a mixture thereof.

12. The thermoplastic film of claim 1, at least
10 one layer is selected from the group consisting of high density polyethylene, medium density polyethylene, low density polyethylene, linear low density polyethylene, polypropylene or blends thereof.

13. A process for producing a thermoplastic film
15 having substantially increased wettability comprising:
partially flourinating a mono, bi or multi
layered polyolefin film by exposing one or more
surfaces of the polyolefin film to flourine and oxygen.

20

14. The process of claim 13 wherein the film has
a polar surface energy of at least about 15 dynes per
centimeter.

15. The process of claim 13 wherein the film is
25 exposed to oxygen in the form of air.

16. The process of claim 13 further comprising
affixing an ink, dye, pigment or coloring agent to the
30 partially flourinated film.

35

17. The process of claim 13 further comprising
coating an adhesive composition onto the partially
flouinated film.

18. The process of claim 13, wherein the
flourinated surface(s) has a flourine:carbon surface

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stoichiometry as determined by x-ray photoelectron spectroscopy of from about 0.001 to about 3.0.

19. The process of claim 13 further comprising
5 printing ink on the partilly flourinated film.

20. The process of claim 13 further comprising coextruding the film with a second polyolefin.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/05273

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08J7/12 B32B27/32 //C08L23:02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,83 03419 (BATTELLE DEVELOPMENT CORPORATION) 13 October 1983 see claims 1,5 see page 3, line 4 - line 8 see page 4, line 17 - line 26 ---	1,3,12, 13,15
X	WO,A,84 00312 (USA, SECRETARY OF COMMERCE) 2 February 1984 see claims 1,2,6-11,13,18,19 see claims 24,25,27,28 see page 12, line 24 - line 26; examples --- -/-	1,2,8,9, 12,13, 14,17,18

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

3 December 1993

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Name and mailing address of the ISA

European Patent Office, P.B. 3818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Niaounakis, M

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/05273

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 88-081842[12] & JP, A, 63035632 (KURARAY KK.) 16 February 1988 see abstract ----	1,3,8,9, 12,13, 15,17,18
X	EP, A, 0300385 (AIR PRODUCTS AND CHEMICALS, INC.) 25 January 1989 see claims 1,14 see page 4, line 13 - line 22 see page 4, line 28 - line 30 ----	1,3,4,12,13, 15,17
A	DE, A, 2412025 (AIR PRODUCTS AND CHEMICALS, INC.) 19 September 1974 see claims 1-3 see page 2, line 13 - line 23 see page 5, line 5 - line 13 ----	1,3,12,13
A	DE, A, 4006809 (ALKOR GMBH KUNSTOFFE) 12 September 1991 see claims 1,6 see examples 1-3 -----	1,2,4, 10-14,20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/05273

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DE-A-4006809	12-09-91	NONE	